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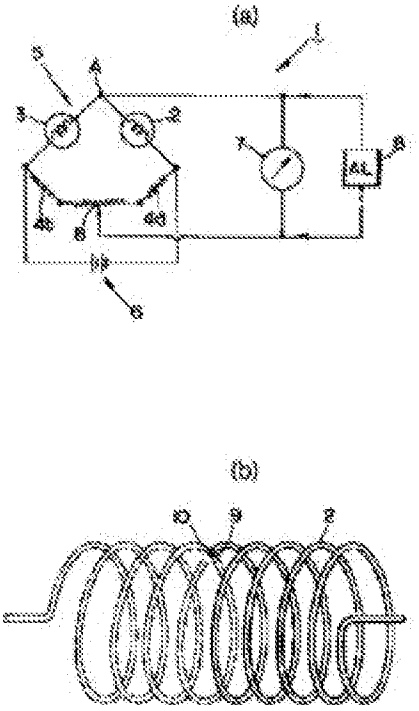
(54) CONTACT COMBUSTION TYPE GAS SENSOR



(57)Abstract:
PROBLEM TO BE SOLVED: To provide a contact combustion type gas sensor wherein an enough amount of change in electric resistance to detect a flammable gas is acquired even when temperature of a gas detection element is low, i.e., under 300°C.
SOLUTION: A contact combustion type gas sensor 1 has, as a gas detection element 2, an electric resistor 9 comprizing a metal, surface of which is coated with platinum or palladium 10. A flammable gas which is in contact with the gas detection element 2 retained at a predetermined temperature is burnt with platinum or palladium 10 as catalyzer and change in electric resistance of the electric resistor 9 owing to combustion heat of the flammable gas is detected, and thereby concentration of the flammable gas is detected. The electric resistor 9 is made of iron or nickel. The electric resistor 9 comprizes iron, surface of which is coated with nickel and further coated, on the nickel coating, with platinum or palladium 10. The gas sensor 1 detects imperfect combustion or non-ignition of a gas apparatus.

CLAIMS

[Claim(s)]
[Claim 1]An electric resistance body which consists of metal which covered the surface with platinum or palladium is used as a gas detection element, This platinum or palladium is made for combustible gas in contact with this gas detection element held at prescribed temperature to burn as a catalyst, A contact burning gas sensor characterized by this electric resistance body being iron or nickel in a contact burning gas sensor which detects concentration of combustible gas by detecting change of electrical resistance of this electric resistance body by combustion heat of this combustible gas.
[Claim 2]The contact burning gas sensor according to claim 1 which said electric resistance body is iron by which the surface is covered with nickel, and is characterized by covering platinum or palladium on covering of this nickel.
[Claim 3]The contact burning gas sensor according to claim 1 or 2, wherein said gas sensor detects incomplete combustion or a misfire of gas fittings.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a contact burning gas sensor.
[0002]
[Description of the Prior Art]In order to detect the incomplete combustion or misfire of gas fittings conventionally, the contact burning gas sensor is known as a means to detect existence of combustible gas. Since the gas detection characteristic continues and is stable at the long period of time as compared with the semiconductor type gas sensor which detects gas by the resistance change of the semiconductor by gas deadsorption of a semiconductor surface, said contact burning gas sensor is widely used as combustible gas, especially an object for detection of carbon monoxide.
[0003]Said conventional contact burning gas sensor uses as a gas detection element the electric resistance body which consists of a platinum wire which covered the surface with platinum or palladium. If combustible gas contacts where such a gas detection element is held at prescribed temperature, this combustible gas will burn considering said platinum or palladium as a catalyst, said electric resistance body will be heated by the combustion heat, and electrical resistance will change. Then, the concentration of combustible gas is detected by energizing to said electric resistance body and detecting the variation of the electrical resistance at the time of heating of said said electric resistance body.
[0004]When combustible gas contacts said gas detection element, in order to make it easy to improve catalytic activity and to burn, as for said contact burning gas sensor, said gas detection element is held at the temperature of not less than 300 **. However, said contact burning gas sensor has a problem that gas detection sensitivity falls remarkably, when the hair spray which contains silicone oil in the interior of a room in which gas fittings are installed is used or silicone is used for the sealing compound of the gas piping of these gas fittings.
[0005]Said problem contacts said gas detection element by which the silicone of low

polymerization degrees, such as silicone oil, is held at the temperature of not less than 300 **, The surface of said catalyst is covered with the silicon dioxide of the glassiness which it started, and the generated high-polymer silicone or this silicone oxidized under the elevated temperature further, and generated the polymerization reaction, and it thinks because contact with said catalyst and said combustible gas is intercepted. Then, in order to solve said problem, it is possible that it uses said contact burning gas sensor as the temperature of said gas detection element will not be not less than 300 **.

[0006]However, by the conventional contact burning gas sensor used as a gas detection element, the electric resistance body which consists of a platinum wire which covered the surface with platinum or palladium. There is inconvenience that the variation of sufficient electrical resistance to detect existence of combustible gas when the temperature of a gas detection element is the low temperature below 300 ** is not obtained.

[0007]

[Problem to be solved by the invention]This invention cancels this inconvenience and an object of this invention is to provide the contact burning gas sensor from which the variation of sufficient electrical resistance to detect existence of combustible gas also when the temperature of a gas detection element is the low temperature below 300 ** is obtained.

[0008]

[Means for solving problem]In order to attain this purpose, the contact burning gas sensor of this invention, The electric resistance body which consists of metal which covered the surface with platinum or palladium is used as a gas detection element, This platinum or palladium is made for the combustible gas in contact with this gas detection element held at prescribed temperature to burn as a catalyst, In the contact burning gas sensor which detects the concentration of combustible gas, this electric resistance body is characterized by being iron or nickel by detecting change of the electrical resistance of this electric resistance body by the combustion heat of this combustible gas.

[0009]Since iron or nickel with a larger rate of change by the temperature of electrical resistivity than platinum is used as an electric resistance body according to this means, also when temperature of this gas detection element is made into the low temperature below 300 **, change of sufficient electrical resistance to detect existence of combustible gas can be obtained.

[0010]Although said electric resistance body fabricates a small-gage wire to a coiled form and it is used, In the contact burning gas sensor of this invention, when said electric resistance body is iron, By having composition with which the surface is covered with nickel and platinum or palladium is further covered on covering of this nickel, even if iron oxidizes by an intermittent periodic duty and resistance becomes high, the open circuit by generation of heat at the time of energization can be prevented.

[0011]Since it is a sensor which detects carbon monoxide, hydrogen, and combustible gas, the contact burning gas sensor of this invention is suitably used, in order to detect the incomplete combustion or misfire of gas fittings which uses town gas or liquefied petroleum gas (LPG) as fuel.

[0012]

[Mode for carrying out the invention]Next, it explains in more detail about one form of enforcement of this invention, referring to attached Drawings. The circuit diagram in which drawing 1 (a) shows the circuitry of the contact burning gas sensor of this invention, the perspective view in which drawing 1 (b) shows the partial section of the gas detection element of the drawing 1 (a) **, and drawing 2 are graphs which show the relation of the metaled electrical resistivity and temperature used as an electric resistance body.

[0013]Like the drawing 1 (a) **, the contact burning gas sensor 1 of this invention is provided with the following.
Are used in order to detect the incomplete combustion or misfire of gas fittings which uses town gas or liquefied petroleum gas (LPG) as fuel, and the circuitry, The power supply 6 which supplies electric power to the bridge 5 while the gas detection element 2 and the temperature compensation element 3 form the bridge 5 with other resistance 4a and 4b.
Gas concentration directions meter 7 in which the gas concentration detected by the gas detection element 2 is shown.
The alarming means 8 which generates an alarm when the concentration of the detected gas exceeds a predetermined standard.
Said gas concentration directions meter 7 is connected to the stationary contact A and movable ** B of the bridge 5, and said alarming means 8 is connected in parallel with the gas concentration directions meter 7.
[0014]Said gas detection element 2 is provided with the enveloping layer 10 of the platinum formed in the surface of the electric resistance body 9 which fabricated the metaled small-gage wire to the coiled form of electroplating etc. like the drawing 1 (b) **, or palladium. In the contact burning gas sensor 1 of this invention, iron (Fe) or nickel (nickel) is used as said electric resistance body 9.
[0015]Like **2**, at the temperature of not less than 200 **, since change by the temperature of electrical resistivity is larger than platinum (Pt), iron and nickel fit said electric resistance body 9 of said gas detection element used at the temperature below 300 **. As iron used for said electric resistance body 9, a thing like 99.5% of purity can be mentioned, for example. As nickel used for said electric resistance body 9, a thing like 99.7% of purity can be mentioned, for example.
[0016]Copper (Cu) of **2** is shown for reference, it is a good conductor, and since change by the temperature of electrical resistivity is smaller than platinum, it is not preferred as said electric resistance body 9.
[0017]Since there is a tendency to oxidize by an intermittent periodic duty and for resistance to become high when said electric resistance body 9 is iron, in order to prevent the open circuit by generation of heat at the time of energization, the surface is covered with nickel and said platinum or palladium is covered on covering of this nickel. Covering of said nickel is stable, and since scaling is prevented, even if it carries out an intermittent periodic duty, iron electrical resistance does not change. Electroless deposition performs nickel covering to iron of said electric resistance body 9, for example.
[0018]In order to prevent an open circuit of said iron, like covering of said nickel, What is necessary is just to constitute the film which can prevent oxidation on the surface of iron, and the thin film of palladium or platinum may be formed in the surface for covering of said platinum or palladium which is a catalyst, for example, and the platinum black and palladium black as a catalyst may be further made [they may be made to adhere them and] and formed in the surface.
[0019]Next, the operation of said contact burning gas sensor 1 is explained. First, the contact burning gas sensor 1 is in the state where the gas detection element 2 is held at prescribed temperature with the external heater etc. which are not illustrated, supplies electric power to the bridge 5 from the power supply 6, and energizes it to the electric resistance body 9 which consists of a small-gage wire of said metal of the gas detection element 2. Since the gas detection element 2 consists of the electric resistance body 9 which equips the surface with the enveloping layer 10 of platinum or palladium as mentioned above, If combustible gas, such as carbon monoxide, contacts the gas detection element 2 currently held as mentioned

above at prescribed temperature, this combustible gas will burn considering platinum or palladium of said enveloping layer 10 as a catalyst, and resistance of the electric resistance body 9 will change with the combustion heat of this combustible gas.
[0020]Then, the contact burning gas sensor 1 moves the traveling contact B of the bridge 5, and detects the variation of the electrical resistance of the electric resistance body 9 as voltage difference between the points of contact A and B of the bridge 5. Since the electrical resistance variation of the electric resistance body 9 detected as mentioned above is proportional to gas concentration, while the gas concentration converted from said electrical resistance variation is directly shown in the gas concentration directions meter 7, it is outputted to the alarming means 8. If said alarming means 8 is provided with the control means which is not illustrated and the concentration of the detected gas exceeds a predetermined standard, This control means judges it as what incomplete combustion or a misfire generated in said gas fittings, and generates an alarm via auditory means, such as an electronic sound, or visual means, such as a photoelectrical display.
[0021]Next, the embodiment and comparative example of this invention are explained.
[0022]
[Work example 1]Drawing 3 is an explanatory sectional view showing the composition of the experimental device for measuring the gas detection performance of a gas detection element of using for a contact burning gas sensor, Drawing 4 thru/or drawing 6 are graphs which show the relation between the carbon monoxide concentration in the gas detection element of the embodiment of this invention, and a comparative example, and the variation of an electric resistance value, and, as for drawing 4, in the case of the gas detection element of Embodiment 1, in the case of the gas detection element of Embodiment 2, drawing 6 shows the case of the gas detection element of a comparative example, respectively, as for drawing 5. Drawing 7 thru/or drawing 10 are graphs for which the relation between the carbon monoxide concentration of the contact burning gas sensor of each embodiment at a predetermined temperature and a comparative example and the variation of an electric resistance value is shown, and, as for drawing 8, in drawing 7, in the case of 230 **, drawing 9 shows [in the case of 300 **] the case of 400 **, respectively in the case of 350 **, as for drawing 10.
[0023]A coiled nickel wire (99.7% of purity) 0.1 mm in diameter and 100 mm in length was prepared, and platinum black covered the surface in this example.
[0024]Covering by platinum black was performed as follows with the electroplating method. First, said nickel wire was immersed into acetone, and after cleaning ultrasonically for 1 minute and degreasing, it was immersed in the water of ordinary temperature for 1 minute, and rinsed. Next, after immersing said nickel wire in the chromium mixed acid of ordinary temperature for 1 minute and carrying out pickling, it was immersed in the water of ordinary temperature for 1 minute, and rinsed.
[0025]Next, supply the hexachloroplatinic acid solution of ordinary temperature to the electroplating tub provided with the electrode as a plating solution, and said nickel wire washed as mentioned above is immersed in this plating solution, While impressing the voltage of 5V between this nickel wire and said electrode, the surface of said nickel wire was covered with platinum black by performing twice operation which energizes 0.4-15.5-mA current for 3 minutes. Next, the nickel wire covered with said platinum black was immersed in the water of ordinary temperature for more than 1 minute, and was rinsed.
[0026]Next, supply 1N sulfuric acid to the cell provided with the electrode as an electrolysis solution, and the nickel wire covered with said platinum black is immersed in this electrolysis solution, While impressing the voltage of 5V between this nickel wire and said

electrode, by performing twice operation which energizes 0.5-15-mA current for 1 minute, electrolytic cleaning of said nickel wire was carried out.
[0027]Next, the nickel wire covered with said platinum black was immersed in the water of ordinary temperature for more than 1 minute, and was rinsed, and after acetone replaced the water adhering to said nickel wire, it dried by warm air. By said electroplating, 0.9-1.1 mg of platinum black has adhered to the surface of said nickel wire.
[0028]Next, heat treatment which holds the nickel wire covered with said platinum black at 400 ** under decompression of a 10^{-3} toll for 1 hour was performed, and the gas detection element 2 of the drawing 1 (b) ** was manufactured.
[0029]Next, the gas detection performance of said gas detection element 2 was evaluated using the equipment of **3**. It assumes that the equipment of **3** uses the gas detection element 2 for drawing 1 (a) and the contact burning gas sensor 1 of the drawing 1 (b) **, The carbon monoxide detection performance of the gas detection element 2 held at prescribed temperature is measured, and it consists of the sealed mullite pipe 11 holding said gas detection element 2, and the electric furnace 12 which accommodates the mullite pipe 11.
[0030]The mullite pipe 11 equips one mouth 11a with the carbon monoxide introduction means 13 and the air introducing means 14 as combustible gas, and the carbon monoxide analyzer 15 is connected to the mouth 11b of another side. The thermometer 16 which measures the temperature of the gas detection element 2 is connected to one mouth 11a.
[0031]The electric furnace 12 is provided with the PID temperature controller 17, and can adjust the temperature in a furnace now. Said gas detection element 2 is connected to the constant current source 18 via the mouths 11a and 11b of the mullite pipe 11.
The voltmeter 20 is connected with the gas detection element 2 in series at the ammeter 19 and parallel.

[0032]The gas detection performance of said gas detection element 2 is in the state which held the temperature of the gas detection element 2 with said electric furnace 12 in each temperature of 230 **, 300 **, 350 **, and 400 **, First, the electrical resistance (R_1) of the electric resistance body 9 at said each temperature was searched for by measuring the voltage of gas detection element 2 both ends when 10-mA constant current is sent through the gas detection element 2 from the constant current source 18 in the air with the voltmeter 20.
[0033]Next, at said each temperature by the carbon monoxide introduction means 13 and the air introducing means 14. Carbon monoxide, respectively 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm of air mixed 2500 ppm is introduced in the mullite pipe 11, After fully replacing the atmosphere in the mullite pipe 11 with the air of one carbon monoxide each concentration, inflow gas was intercepted and the electrical resistance (R_2) of the electric resistance body 9 corresponding to said one carbon monoxide each concentration was searched for by the completely same method as the above. And the electrical resistance (R_2) of the electric resistance body 9 in the inside of the air which carbon monoxide mixed at said given temperature, The difference with the electrical resistance (R_1) in the inside of the air which does not contain carbon monoxide was searched for, and the electrical resistance variation (deltaR=R_2-R_1, unit:momega) of the electric resistance body 9 corresponding to carbon monoxide concentration was calculated. A result is shown in the following table 1 and drawing 4.
[0034]
[Table 1]

		温度 (℃)			
		230	300	350	400
CO濃度 (ppm)	0	0	0	0	0
	500	- 0.15	- 0.79	6.17	6.75
	1000	4.66	9.26	8.61	11.92
	1500	8.44	8.53	15.37	14.90
	2000	12.59	13.85	14.19	20.91
	2500	18.87	23.21	21.21	20.65

[0035]
[Work example 2]A coiled low carbon steel wire (99.7% of purity) 0.1 mm in diameter and 100 mm in length was prepared, the surface was first covered with nickel, and, subsequently to the covering top of this nickel, platinum black was further covered with this example.
[0036]Covering by nickel was performed as follows by the electroless deposition method. First, said low carbon steel wire was immersed into acetone, and after cleaning ultrasonically for 1 minute and degreasing, it was immersed in the water of ordinary temperature for 1 minute, and rinsed. Next, after immersing said low carbon steel wire in the 20% chloride of ordinary temperature for 1 minute and carrying out pickling, it was immersed in the water of ordinary temperature and rinsed within 1 minute.
[0037]Next, the surface of said low carbon steel wire was covered with nickel by immersing said low carbon steel wire into 80 ** electroless nickel plating liquid for 1 hour, and carrying out electroless deposition. Next, the low carbon steel wire covered with said nickel was immersed in the water of ordinary temperature for more than 5 minutes, and was rinsed, after performing operation in which acetone replaces the water adhering to said low carbon steel wire, for 2 minutes, it dried by warm air, and the low carbon steel wire covered with nickel was obtained. By said electroless deposition, 0.4 mg of nickel has adhered to the surface of said low carbon steel wire smoothly by a thickness of 1.2 micrometers.
[0038]Next, the completely same electroplating method as the nickel wire of Embodiment 1 covered the surface of the low carbon steel wire covered with said nickel by platinum black. By said electroplating, 0.9-1.1 mg of platinum black has adhered on said nickel covering.
[0039]Next, after performing heat treatment which holds the low carbon steel wire in which covering of platinum black was further given on said nickel covering at 400 ** under decompression of a 10^{-3} toll for 1 hour, it annealed at 400 ** and the gas detection element 2 of the drawing 1 (a) ** was manufactured.
[0040]Next, the completely same method as Embodiment 1 estimated the gas detection performance of said gas detection element 2 using the equipment of **3**. A result is shown in the following table 2 and drawing 5.
[0041]
[Table 2]

		温度 (℃)			
		230	300	350	400
CO濃度 (ppm)	0	0	0	0	0
	500	6.14	1.46	9.86	10.59
	1000	4.08	4.66	9.32	15.45
	1500	11.11	11.21	12.01	18.34
	2000	12.10	14.47	17.79	22.55
	2500	20.81	17.66	29.75	34.95

[0042]
[Comparative Example(s)]At this example, a coiled platinum wire 0.1 mm in diameter and 100 mm in length was prepared, and the completely same electroplating method as the nickel wire of Embodiment 1 covered the surface by platinum black. By said electroplating, 0.9-1.1 mg of platinum black has adhered to the surface of said platinum wire.
[0043]Next, heat treatment which holds the platinum wire covered with said platinum black at 400 ** under decompression of a 10^{-3} toll for 1 hour was performed, and the gas detection element 2 of the drawing 1 (a) ** was manufactured.
[0044]Next, the completely same method as Embodiment 1 estimated the gas detection performance of said gas detection element 2 using the equipment of **3**. A result is shown in the following table 3 and drawing 6.
[0045]
[Table 3]

		温度 (℃)			
		230	300	350	400
CO濃度 (ppm)	0	0	0	0	0
	500	1.41	6.76	- 1.57	5.24
	1000	1.49	4.92	5.40	7.41
	1500	5.75	5.86	7.01	4.27
	2000	4.49	5.52	6.81	11.29
	2500	7.64	9.07	7.53	14.64

[0046]According to the gas detection element 2 of said each embodiment from said tables 1-3 and drawing 4 - the data of six, and a comparative example. If the electrical resistance variation of the electric resistance body 9 has the low concentration of carbon monoxide almost corresponding to the concentration of carbon monoxide, its electrical resistance variation is also small, and if the concentration of carbon monoxide is high, it is clear that electrical resistance variation is also large and can be used for a contact burning gas sensor.
[0047]Said tables 1-3 and drawing 4 - the data of six were carried out according to said each temperature, and were gathered in drawing 7 - 10. From drawing 7, even when maintained by the temperature below 300 ** of 230 ** according to the gas detection element 2 of said Embodiment 1 and Embodiment 2, carbon monoxide of 2500 ppm or less is received, It is clear that the variation of electrical resistance with the bigger electric resistance body 9 than the gas detection element 2 (comparative example) which consists of platinum is obtained.

Therefore, according to the gas detection element 2 of said Embodiment 1 and Embodiment 2, combustible gas, such as carbon monoxide, is detectable in the temperature requirement where the polymerization reaction of silicone does not advance easily.
[0048]It is clear that the variation of bigger electrical resistance than the gas detection element 2 of said comparative example is obtained from drawing 8 thru/or drawing 10 except for the case where carbon monoxide of 1000 ppm or less when maintained by 300 ** is received according to the gas detection element 2 of said Embodiment 1 and Embodiment 2.
[0049]Although platinum (platinum black) has covered the electric resistance body 9 in said each embodiment, it may be made to cover with palladium.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]As for drawing 1 (a), drawing 1 (b) is a circuit diagram showing the circuitry of the contact burning gas sensor of this invention, and a perspective view showing the partial section of the gas detection element of the drawing 1 (a) **.
[Drawing 2]The graph which shows the relation of the metaled electrical resistivity and temperature used as an electric resistance body.
[Drawing 3]The explanatory sectional view showing the composition of the equipment which measures the gas detection performance of a gas detection element.
[Drawing 4]The graph which shows the relation between the carbon monoxide concentration in the gas detection element of Embodiment 1 of this invention, and the variation of an electric resistance value.
[Drawing 5]The graph which shows the relation between the carbon monoxide concentration in the gas detection element of Embodiment 2 of this invention, and the variation of an electric resistance value.
[Drawing 6]The graph which shows the relation between the carbon monoxide concentration in the conventional gas detection element 2, and the variation of an electric resistance value.
[Drawing 7]The graph which shows the relation between carbon monoxide concentration when a gas detection element is maintained at 230 **, and the variation of an electric resistance value.
[Drawing 8]The graph which shows the relation between carbon monoxide concentration when a gas detection element is maintained at 300 **, and the variation of an electric resistance value.
[Drawing 9]The graph which shows the relation between carbon monoxide concentration when a gas detection element is maintained at 350 **, and the variation of an electric resistance value.
[Drawing 10]The graph which shows the relation between carbon monoxide concentration when a gas detection element is maintained at 400 **, and the variation of an electric resistance value.
[Explanations of letters or numerals]
1 [-- Platinum or palladium.] -- A contact burning gas sensor and 2 -- A gas detection element and 9 -- An electric resistance body and 10

[Translation done.]

DRAWINGS

[Drawing 1]

FIG. 1(a)

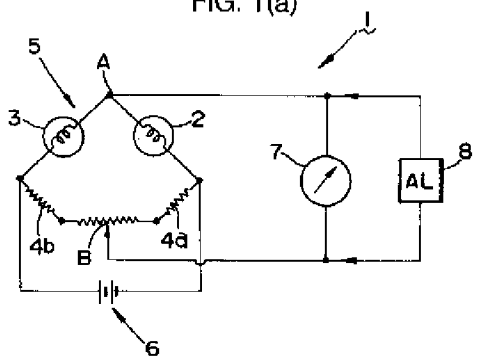
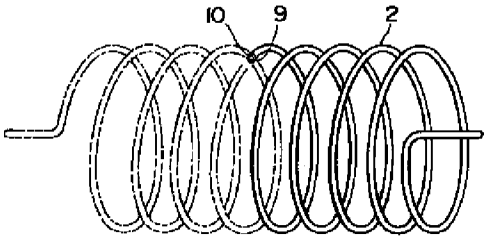
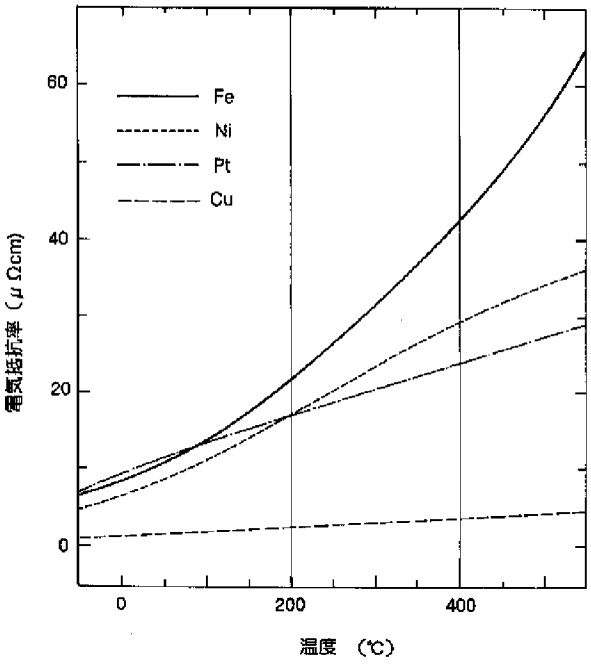


FIG. 1(b)



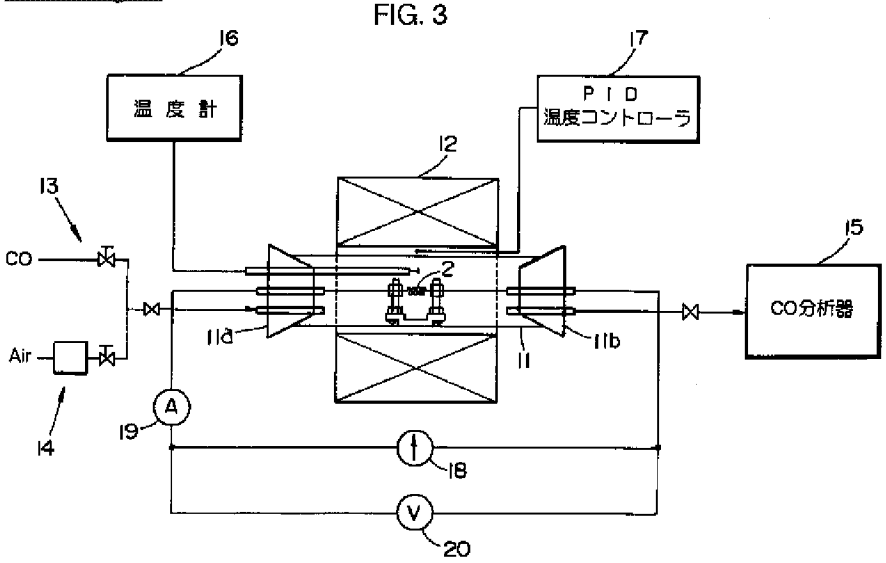
[Drawing 2]

FIG. 2



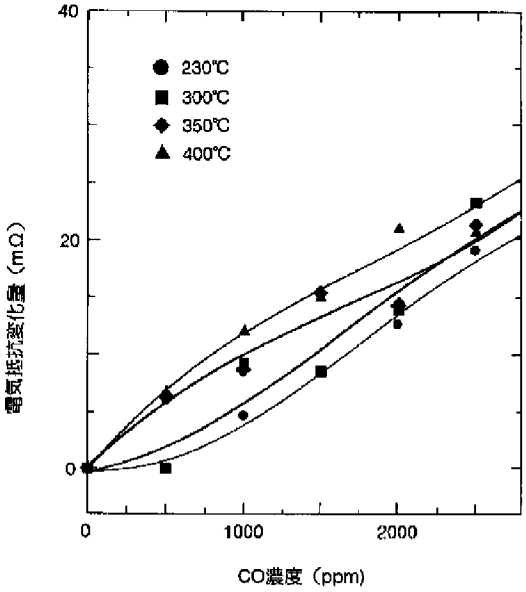
[Drawing 3]

FIG. 3



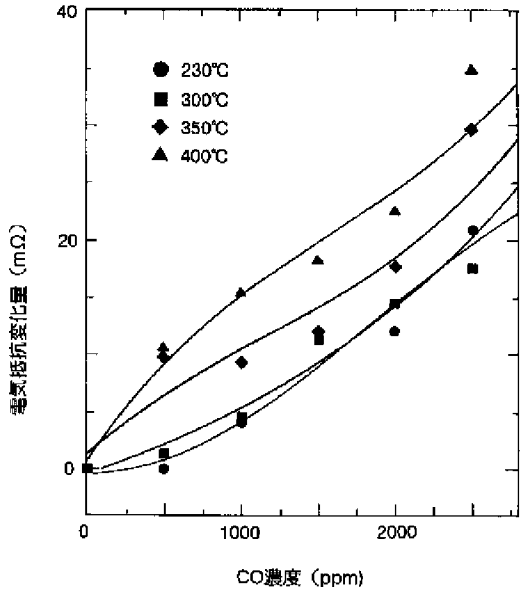
[Drawing 4]

FIG. 4



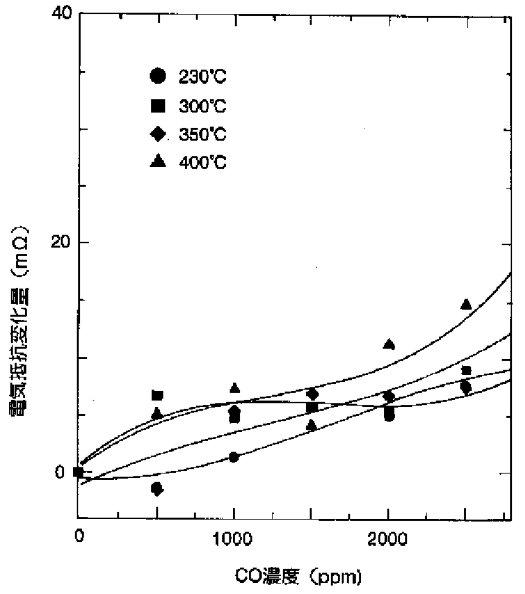
[Drawing 5]

FIG. 5



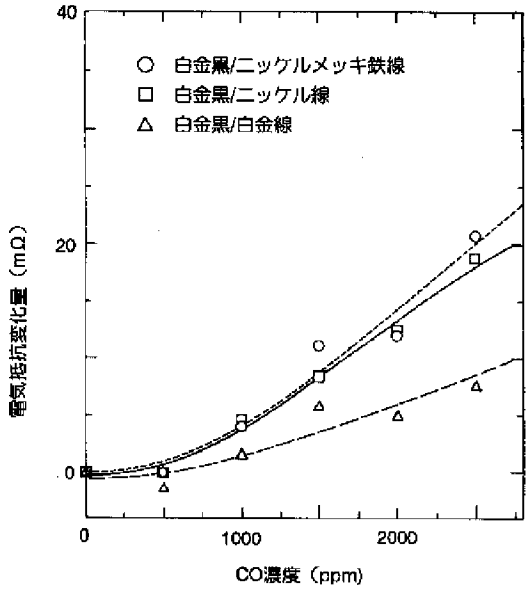
[Drawing 6]

FIG. 6



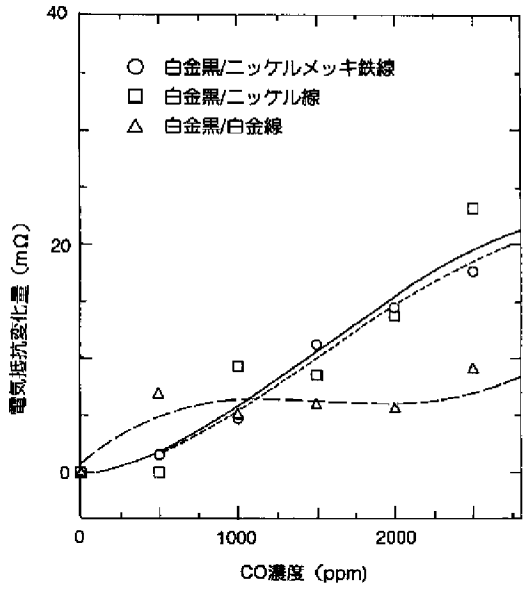
[Drawing 7]

FIG. 7



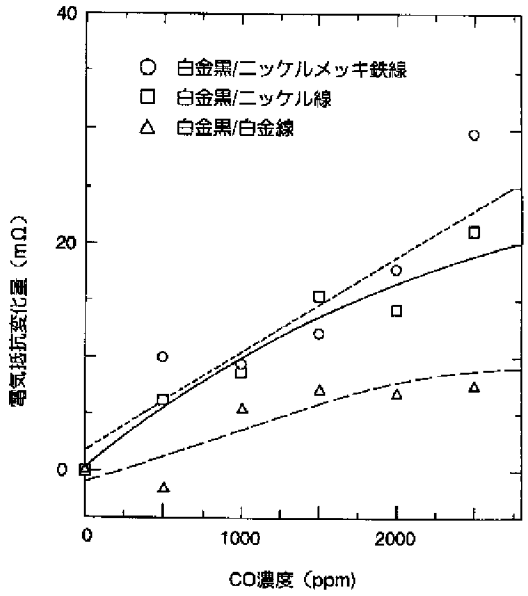
[Drawing 8]

FIG. 8



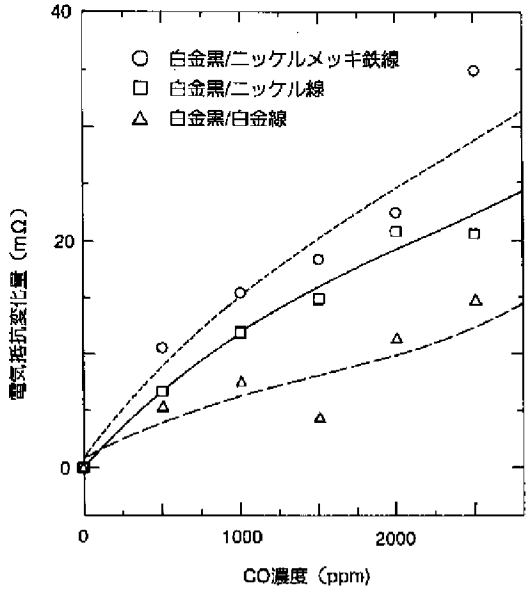
[Drawing 9]

FIG. 9



[Drawing 10]

FIG. 10



[Translation done.]